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Influence of synthetic parameters and reaction conditions on properties of $Ce_xZr_{1-x}O_2$ for CO preferential oxidation reaction in H_2-rich gases

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Abstract

$Ce_xZr_{1-x}O_2$ (x=0-1) catalysts were prepared by urea grind combustion method (UGC) and tested for CO preferential oxidation in H_2-rich gases. The catalytic performances of $Ce_xZr_{1-x}O_2$-UGC-400 are comparable to $Ce_xZr_{1-x}O_2$-SG-400 and higher than $Ce_xZr_{1-x}O_2$-SA-400. The optimal Ce/Zr molar ratio, calcination temperature and urea addition (R value) for synthesizing $Ce_xZr_{1-x}O_2$ catalysts are Ce/Zr = 4:1, 300 °C and R = 1.0, respectively. $Ce_{0.8}Zr_{0.2}O_2$ catalyst prepared with this route can well adapt the change of gas hourly space velocity (GHSV), and no any obvious change is observed both in CO conversion and O_2 selectivity with GHSV increasing from 12000 to 48000 h^{-1}. Both CO conversion and O_2 selectivity of $Ce_{0.8}Zr_{0.2}O_2$ maintains relative stability during 72 h time-on-stream test.

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Keywords: $Ce_xZr_{1-x}O_2$; Ce-Zr-O_2 solid solution; calcination temperature; urea addition.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been regarded as one of the most attractive clean alternatives to conventional combustion of fossil fuels to generate energy due to the advantages of high efficiency, large power density as well as low operating temperature. However, the trace amount of CO in raw gas of H_2, which

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is generally arisen from fossil fuels via catalytic conversion such as low temperature water gas shift, can result in easy poisoning of the anode materials of PEMFCs. Therefore, various strategies have been developed to remove the trace amount of CO in H_2-rich gases. Among them, the CO preferential oxidation reaction (CO-PROX) has attracted considerable attention due to its simplicity and high efficiency for purifying H_2-rich gases.

Cerium dioxide is of great interest because of its oxygen storage and release properties [1]. However, the pure CeO_2 has poor thermal stability. Recently, Ce-Zr-O_2 solid solutions are extensively used in catalysis compared with CeO_2 [2]. Incorporation of Zr^{4+} into the lattice CeO_2 can modify the structure of CeO_2 crystallite to form a Ce-Zr-O_2 solid solution, which leads to the enhancement of oxygen storage capacity (OSC) of CeO_2, redox property, thermal resistance and the promotion of metal dispersion [3-5], thus resulting in the improvement of catalytic performances for many reaction such as CO oxidation [6] and combustion of methane [7].

The catalyst preparation method, which would result in different structural and textural properties, plays an important role in the catalytic performance. Therefore, numerous methods, such as co-precipitation method [8,9], sol-gel technique [10], surfactant-assisted method [11] have been developed to prepare Ce-Zr-O_2 catalyst. Cao et al [12] investigated the activities of $CuO/Ce_{0.8}Zr_{0.2}O_2$ catalysts synthesized by using three methods for CO removal from hydrogen-rich gas. They found that the $CuO/Ce_{0.8}Zr_{0.2}O_2$ catalysts prepared by surfactant-assisted method possess mesoporous framework with narrow pore size distribution, uniform distribution of nanoscale particle size and high specific surface area and exhibited the best catalytic performance. These traditional methods can obtain the desired results, but the process of preparation is complex and time-consuming.

In this work, we reported that a facile route to synthesize $Ce_{0.8}Zr_{0.2}O_2$ by urea grind combustion method (UGC), and the effects of synthetic parameters (the molar ratio of Ce/Zr, calcination temperature as well as the addition of urea) and reaction condition (gas hourly space velocities, GHSV) on the catalytic performance of $Ce_xZr_{1-x}O_2$(with x=0-1) for CO preferential oxidation reaction in H_2-rich gases were investigated in detail.

2. Experimental

2.1 Catalyst preparation

The $Ce_xZr_{1-x}O_2$ catalysts synthesized by using urea grind combustion method were briefly described as follows: the calculated amount of $Ce(NO_3)_3 \cdot 6H_2O$, $Zr(NO_3)_4 \cdot 5H_2O$ and $(NH_2)_2CO$ were mixed and grinded in agate mortar under room temperature until the transparent viscous gel was obtained. After that the gel was calcined at 400^oC for 20min. In order to investigate the effect of calcination temperature, the gel was calcined at 300^oC and 500^oC, respectively. All the catalysts synthesized with this route are denoted as $Ce_xZr_{1-x}O_2$-UGC-M (or $Ce_xZr_{1-x}O_2$-M), where "M" is the calcination temperature and "x" is the Ce content calculated on the basis of Ce/Zr molar.

For comparison purposes, $Ce_xZr_{1-x}O_2$ samples were also prepared by using surfactant-assisted and sol-gel methods according to the recipes and procedures reported in Reference [12], and the corresponding catalysts calcined at 400 ^oC were designated $Ce_xZr_{1-x}O_2$-SA-400 and $Ce_xZr_{1-x}O_2$-SG-400, respectively.

2.2 Catalytic activity measurement

Selective CO oxidation in hydrogen-rich gas was carried out in a tubular reactor under atmospheric pressure. 150 mg of catalyst diluted with quartz sands (both in 40-60 mesh) was loaded in quartz tubular reactor with an inner diameter of 6mm. A K-type thermocouple was inserted into the catalyst bed to monitor reaction temperature. The typical feed gas mixture of 1%CO, 1%O_2, 50% H_2 in volume and with He as balance gas, and the total gas flow rate was 80ml/min, corresponding to a space velocity (S.V.) of 16000 h^{-1}. The exit gases from the reactor were analysed by on-line gas chromatography (Fu Li 9790) with a thermal conductivity detector (TCD), a hydrogen flame ionization detector (FID) together with a methanation reactor. The catalytic activity is expressed in terms of the CO conversion (%) and O_2 (%) selectivity, which were calculated based on the CO consumption, as shown below:

$$\text{CO conversion}(\%) = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100 \quad (1)$$

$$O_2 \text{ selectivity } (\%) = \frac{0.5\times([CO]_{in} - [CO]_{out})}{[O_2]_{in} - [O_2]_{out}} \times 100 \quad (2)$$

Where $[CO]_{in}$ and $[CO]_{out}$ are the concentrations of CO(%(v/v))in the feedstream and the effluent, respectively, $[O_2]_{in}$ and $[O_2]_{out}$ are the concentrations of O_2(%(v/v)) in the feedstream and the effluent, respectively.

2.3 Catalyst characterization

N_2 adsorption-desorption isotherms were carried out on a Quantachrome NOVA 2000e sorption analyzer at -196 ^oC. All samples were was degassed at 200 ^oC for 6h prior to analysis. BET specific surface area was calculated from adsorption data in the relative pressure ranging from 0.05 to 0.25. X-ray diffraction (XRD) patterns were performed on a Rigaku D/max-1200 diffractometer by using Cu Ka radiation (λ=1.5406 Å) at 2θ range between 10 and 90 ^{o} with a step width of 0.02^o. H_2-TPR was performed in an in-house constructed system equipped with a thermal conductivity detector (TCD) to measure H_2 consumption. Prior to H_2-TPR analysis, a quartz tube was loaded with 100 mg of catalyst which was pretreated at 400 ^oC for 60 min with 5 vol% O_2 / Ar mixture gas and was cooled to 100 ^oC in the flow of ultra-pure argon gas. After that, the sample was heated in the flow of 10 vol % H_2/Ar mixture gas from 100 to 900 °C at a ramp rate of 10 °C/min.

3. Results and discussion

3.1 Influence of different methods

Catalytic performances of $Ce_{0.8}Zr_{0.2}O_2$ samples prepared by three different methods were tabulated in Table 1. As can be seen by comparing Table 1, CO conversion and O_2 selectivity of $Ce_{0.8}Zr_{0.2}O_2$-UGC-400 are higher than those of $Ce_{0.8}Zr_{0.2}O_2$-SA-400. It is also noted that the catalytic performances of $Ce_{0.8}Zr_{0.2}O_2$-UGC-400 are comparable to and slightly higher than $Ce_{0.8}Zr_{0.2}O_2$-SG-400 when the reaction temperature is blew and above 450 ^oC, respectively. A perfect example can be found that the maximum CO conversion of $Ce_{0.8}Zr_{0.2}O_2$-SG-400 and $Ce_{0.8}Zr_{0.2}O_2$-UGC-400 are 75.18% and 74.21% and the corresponding O_2 selectivity of them are 38.47% and 38.71%, respectively.

Table 1 Compare of $Ce_{0.8}Zr_{0.2}O_2$ catalysts prepared with different methods for CO-PROX.

Samples	CO conversion (%)						O_2 selectivity (%)					
	300 ^oC	350 ^oC	400 ^oC	450 ^oC	500 ^oC	550 ^oC	300 ^oC	350 ^oC	400 ^oC	450 ^oC	500 ^oC	550 ^oC
$Ce_{0.8}Zr_{0.2}O_2$-SA-400	12.27	40.17	69.12	53.48	35.51	10.89	60.06	55.04	34.76	26.86	17.71	5.43
$Ce_{0.8}Zr_{0.2}O_2$-SG-400	16.55	48.12	75.18	57.94	34.37	11.54	62.83	59.97	38.47	29.29	17.30	5.79
$Ce_{0.8}Zr_{0.2}O_2$-UGC-400	15.85	46.78	74.21	58.02	42.62	20.97	63.06	58.64	38.71	29.34	21.49	10.56

BET surface area of $Ce_{0.8}Zr_{0.2}O_2$-SA-400, $Ce_{0.8}Zr_{0.2}O_2$-SG-400 and $Ce_{0.8}Zr_{0.2}O_2$-UGC-400 is 111.0, 71.0 and 70.5 m^2g^{-1}, respectively. On the basis of the above results, it can be deduced that BET surface area isn't the main factor to determine the catalytic performances of $Ce_{0.8}Zr_{0.2}O_2$.

Table 2 The BET surface area of three different $Ce_{0.8}Zr_{0.2}O_2$ catalysts

Samples	$Ce_{0.8}Zr_{0.2}O_2$-SA-400	$Ce_{0.8}Zr_{0.2}O_2$-SG-400	$Ce_{0.8}Zr_{0.2}O_2$-UGC-400
BET surface area(m^2g^{-1})	111.0	71.0	70.5

On the basis of the results that catalytic performances of $Ce_{0.8}Zr_{0.2}O_2$-UGC-400 are comparable to and slightly higher than $Ce_{0.8}Zr_{0.2}O_2$-SG-400 when the reaction temperature is blew and above 450 ^oC, respectively. Furthermore, the synthesis route of $Ce_{0.8}Zr_{0.2}O_2$-UGC-400 is far simpler with respect to that of $Ce_{0.8}Zr_{0.2}O_2$-SG-400. Therefore, in following of this paper, other parameters for synthesizing $Ce_{0.8}Zr_{0.2}O_2$ catalysts with this route together with the reaction conditions for testing the corresponding catalysts were further investigated in detail.

3.2 Effect of Ce/Zr molar ratio of for CO selective oxidation

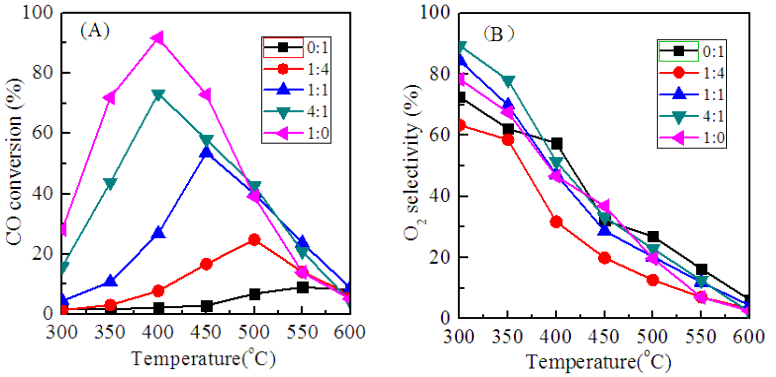

Fig.1 Effect of Ce/Zr molar ratio of $Ce_xZr_{1-x}O_2$ catalysts on the selective oxidation of CO: (A) CO conversion and (B) O_2 selectivity.

The effects of Ce/Zr molar ratio (0:1, 1:4, 1:1, 4:1 and1:0, corresponding to the x value of 0, 0.2, 0.5, 0.8 and 1) on catalytic performances of $Ce_xZr_{1-x}O_2$ catalysts were presented in Fig.1. Obviously, the maximum CO conversion of $Ce_xZr_{1-x}O_2$ increases with the x value, and the corresponding reaction temperature decreases with the x value. A perfect can be found that the maximum CO conversion of $Ce_{0.8}Zr_{0.2}O_2$ is 74.21% at 400 °C and the maximum CO conversion of $Ce_0Zr_{1.0}O_2$ (ZrO_2) is 9.08% at 550 °C. As shown in Fig.1, both $Ce_{0.8}Zr_{0.2}O_2$ and $Ce_{1.0}Zr_0O_2$ (CeO_2) are achieved the maximum CO conversion at 400 °C, while catalytic activity of $Ce_{1.0}Zr_0O_2$ (91.66%) is higher than that of $Ce_{0.8}Zr_{0.2}O_2$ (74.21%). As can be seen by comparing Fig. 1A, $Ce_{0.8}Zr_{0.2}O_2$ exhibits higher catalytic activity than $Ce_{1.0}Zr_0O_2$ when reaction temperature is above 500 °C, which might be closely associated with the formation of Ce-Zr-O_2 solid solutions, thus improving the stability for $Ce_{0.8}Zr_{0.2}O_2$ [13]. Moreover, it also noted that O_2 selectivity of $Ce_{0.8}Zr_{0.2}O_2$ is higher than that of $Ce_{1.0}Zr_0O_2$ in the entire reaction temperature range, thus indicating that the addition of Zr into CeO_2 will promote the redox behaviors (high oxygen storage capacity and mobility of lattice oxygen etc) of $Ce_{0.8}Zr_{0.2}O_2$ with respect to CeO_2. Hence, $Ce_{0.8}Zr_{0.2}O_2$ rather than $Ce_{1.0}Zr_0O_2$ was further investigated in the following of this paper.

3.2 Effect of calcination temperature

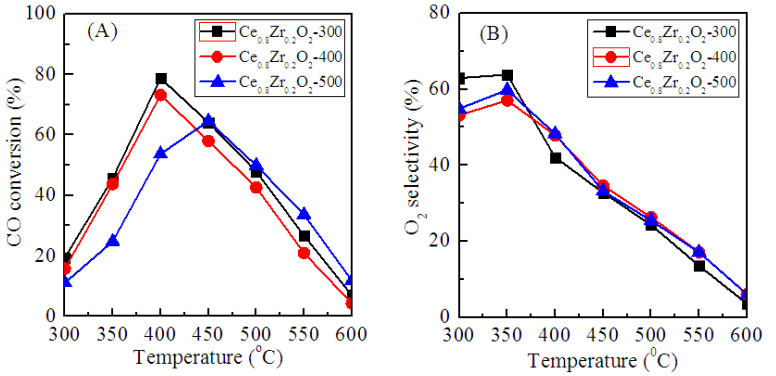

Fig.2 Effect of calcination temperature for $Ce_{0.8}Zr_{0.2}O_2$ catalysts on the selective oxidation of CO: (A) CO conversion and (B) O_2 selectivity.

It was documented that calcination temperature is one of the important factors affecting catalytic performances of catalysts [14-16]. Accordingly, once the optimal Ce/Zr molar ratio was determined for preparing $Ce_xZr_{1-x}O_2$ catalyst ($Ce_{0.8}Zr_{0.2}O_2$), the influence of calcination temperature on the performances of $Ce_{0.8}Zr_{0.2}O_2$ was investigated, and the

corresponding results are presented in Fig. 2. As can be seen by comparing Fig. 2A, CO conversion of the three samples is in the order of $Ce_{0.8}Zr_{0.2}O_2$-300 > $Ce_{0.8}Zr_{0.2}O_2$-400 > $Ce_{0.8}Zr_{0.2}O_2$-500, and the maximum CO conversion of $Ce_{0.8}Zr_{0.2}O_2$-300 (78.79%) and $Ce_{0.8}Zr_{0.2}O_2$-400 (74.21%) was achieved at reaction temperature of 400 °C, while $Ce_{0.8}Zr_{0.2}O_2$-500 exhibits the maximum CO conversion (64.59) at 450 °C. In addition, it is also noted that O_2 selectivity of $Ce_{0.8}Zr_{0.2}O_2$-300 is higher than that of $Ce_{0.8}Zr_{0.2}O_2$-400 and $Ce_{0.8}Zr_{0.2}O_2$-500, especially when reaction temperature is below 350 °C (Fig. 2B). The difference in catalytic performances between $Ce_{0.8}Zr_{0.2}O_2$-300 and $Ce_{0.8}Zr_{0.2}O_2$-400 and $Ce_{0.8}Zr_{0.2}O_2$-500 can be explained according to particle size, oxygen storage capacity together with mobility of lattice oxygen of them (XRD Patterns and H_2-TPR profiles not shown).

Based on the results of calcination temperature, it can be deduecd that the optimal calcination temperature of $Ce_xZr_{1-x}O_2$ catalyst is 300 °C.

3.3 Effect of the addition of urea

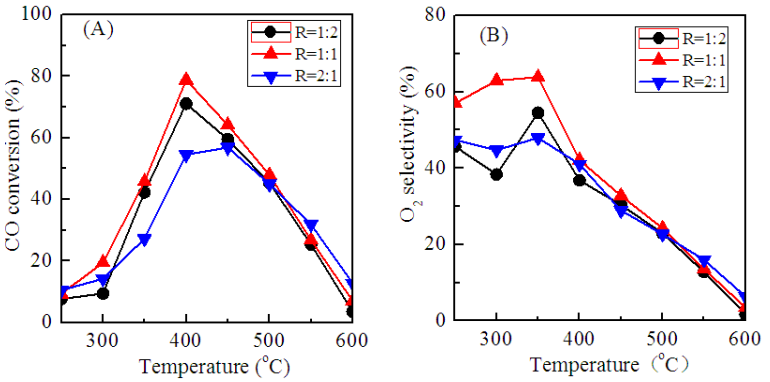

Fig.3 Effect of urea adding for the $Ce_{0.8}Zr_{0.2}O_2$ catalysts on the selective oxidation of CO: (A) CO conversion and (B) O_2 selectivity.

(R represents the ratio of actual addition of urea and theoretical addition of urea)

The theoretical addition of urea according the following chemical equation (Eq. (3)-(4)):

$$6Ce(NO_3)_3 \cdot 6H_2O + 14(NH_2)_2CO = 14CO_2 + 23N_2 + 6CeO_2 + 64H_2O \quad (3)$$

$$6Zr(NO_3)_4 \cdot 5H_2O + 20(NH_2)_2CO = 20CO_2 + 32N_2 + 6ZrO_2 + 70H_2O \quad (4)$$

Herein, R represents the ratio of actual urea addition to theoretical urea addition.

The effects of various urea additions on catalytic performances of $Ce_{0.8}Zr_{0.2}O_2$ catalysts were investigated and the corresponding results are displayed in Fig.3**.** As shown in Fig. 3A, compared with $Ce_{0.8}Zr_{0.2}O_2$ catalysts prepared with R values of 1/2 and 2/1, the catalysts prepared with R value of 1/1 exhibits maximun CO conversion (78.79%) and highest O_2 selectivity (63.82%). The effect of urea addition on catalytic performances of $Ce_{0.8}Zr_{0.2}O_2$ catalysts can be explained as follows: when the addition of urea below the theoretical value is not beneficial to the formation of mesostructure; while the addition of urea beyond the theoretical value would cause sintering and collapse.

3.4 Effect of GHSV

The activity of $Ce_{0.8}Zr_{0.2}O_2$ catalyst was evaluated at three different gas hourly space velocities (GHSV = 12000, 24000 and 48000 h^{-1}), and the results were shown in Fig.4. It is clear that no any obvious change is observed both in CO conversion and O_2 selectivity with GHSV increasing from 12000 to 48000 h^{-1}. This indicates that this catalyst ($Ce_{0.8}Zr_{0.2}O_2$) has a good adaptability of space velocity.

3.5 Stability of $Ce_{0.8}Zr_{0.2}O_2$ catalyst

In order to examine the stability of $Ce_{0.8}Zr_{0.2}O_2$ prepared by urea grind combustion method, a time-on-stream experiment was conducted at operating temperature of 400°C and GHSV of 24000 h^{-1}, as shown in Fig.5. Both CO conversion and O_2 selectivity of $Ce_{0.8}Zr_{0.2}O_2$ maintains relative stability during 72 h time-on-stream test, thus suggesting $Ce_{0.8}Zr_{0.2}O_2$ prepared by urea grind combustion method has excellent stability.

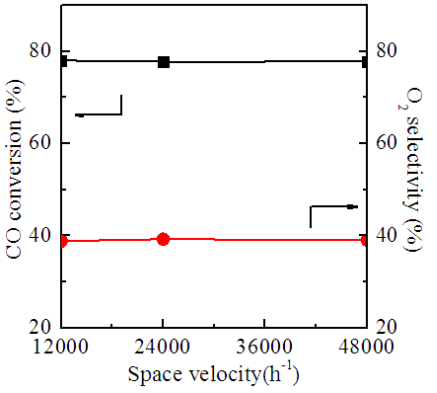

Fig.4 Effect of space GHSV on $Ce_{0.8}Zr_{0.2}O_2$(calcination temperature at 300°C, R=1:1, reaction temperature at 400°C).

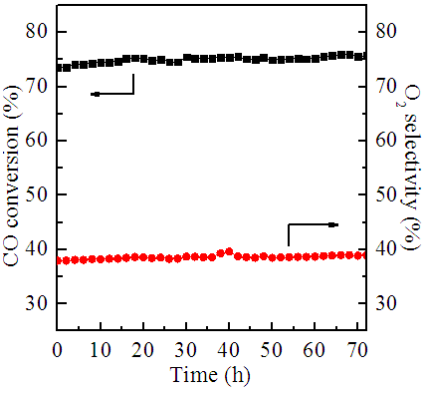

Fig.5 Time-on-stream CO conversion on $Ce_{0.8}Zr_{0.2}O_2$ at 400°C and GHSV of 24000 h^{-1}.

4. Conclusions

Catalytic performances of $Ce_{0.8}Zr_{0.2}O_2$ prepared by urea grind combustion method (UGC) are comparable and higher than that of $Ce_{0.8}Zr_{0.2}O_2$ prepared by surfactant-assisted and sol-gel methods, respectively. The effects of synthetic parameters (Ce/Zr molar ratio, calcination temperature and the addition of urea) on catalytic performances of $Ce_xZr_{1-x}O_2$ were investigated in detail. It was found that the optimal Ce/Zr molar ratio, calcination temperature and urea addition (R value) for synthesizing $Ce_xZr_{1-x}O_2$ catalysts are Ce/Zr = 4:1, 300 °C and R = 1.0, respectively. Furthermore, $Ce_{0.8}Zr_{0.2}O_2$ catalyst prepared with this route exhibits an excellent adaptability of space velocity, and no any obvious change is observed both in CO conversion and O_2 selectivity with GHSV increasing from 12000 to 48000 h^{-1}. Both CO conversion and O_2 selectivity of $Ce_{0.8}Zr_{0.2}O_2$ maintains relative stability during 72 h time-on-stream test.

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